Data Evaluation Record on the adsorption-desorption of MS (5-Chloro-2-methylsulfonyl thiazole) in five soils

MRID Number 48574835

Data Requirement: OECD Guideline: 106
EPA Guideline: 835.1230

EPA PC Code: 050410
DP barcode: 403340

Test material: MS (5-Chloro-2-methylsulfonyl thiazole)

Primary Reviewer: Martin LeMay**,** PMRA

Secondary Reviewers: James Lin, US EPA **EPA Signature:**
Date: February 13, 2013

This study was reviewed as part of a global review. Therefore, the data evaluation was prepared in monograph form. This preface is a supplement to the attached monograph section and documents the review of the study for EFED.

Results Synopsis:
This study is classified as **acceptable**. (The same conclusion as PMRA)

CITATION: Brands C. (2011d) Adsorption/Desorption of MS on five soils. Makhteshim Chemical Works, Ltd. Report No.: R-28475, 20 December 2011 (MRID 48574835)

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Guideline: OECD Guideline No. 106
USEPA guideline 185.1230
Deviations: None

GLP: Yes (laboratory certified by Netherlands VWA Authority)

Executive Summary

The adsorption characteristics of MS (5-chloro-thiazole-2-sulfonic acid) were studied in a batch equilibrium experiment using five soils: a silt loam [Fislis; pH 6.8, organic carbon 2.13%], a sandy loam [Sevelen; pH 7.4; organic carbon 1.61%], a loam [Hom, pH 7.2; organic carbon 2.36%], a loamy sand [Speyer 2.2, pH 5.4; organic carbon 2.16%], and a clay [Speyer 6S, pH 7.2; organic carbon 1.75%]. The adsorption phase was carried out by equilibrating air-dried soil with 5-chloro-2-methylsulfonyl thiazole at nominal concentrations of 0.1, 0.5, 1.0, 2.5 and 10 mg a.i./L for 24 hours at 20 ± 2ºC in the dark. The desorption phase of the study was carried out by replacing the adsorption solution with an equivalent volume of 0.01 $CaCl_2$ and equilibrating for 24 hours. Adsorption equilibrium was reached after 24 hours, but no clear desorption equilibrium was reached. Post desorption soils of Fislis, Sevelen and Horn were extracted with 50/50 (v/v) acetonitrile/water. Adsorption and desorption solutions and soil extracts were analyzed by LC/MS method. Mass balances for Fislis, Sevelen and Horn systems as sum of test substances in adsorption and desorption solutions and soil extracts ranged from 95% to 106% of the applied.

Following 24 hours of equilibration, an average of 11.0% of the applied test substance was adsorbed to the Fislis silt loam, 8.7% to the Sevelen sandy loam, 21.9% to the Horn loam, 20.9% to the Speyer 2.2 loamy sand and 27.9% to the Speyer 6S clay. Linear regression determined K_{adsd} values were 0.306, 0.282, 0.649, 0.568, and 0.884 for the Fislis, Sevelen, Horn, Speyer 2.2 and Speyer 6S, respectively; corresponding $K_{ads\ OC}$ values were 14.3, 17.5, 27.5, 26.3 and 50.5, respectively. Determined $K_{ads\ FOC}$ values ranged from 11.4 to 47.4 (averaged $K_{ads\ FOC}$ was 25.5 and 1/n was 0.947) indicating that MS is very mobile in soil. Adsorption coefficients of MS was independent of % organic carbon, pH and clay content.

Following 24 hours of a single desorption cycle, the average percent of MS desorbed from the test soils was 48.6%, 39.3%, 34.3%, 42.8% and 36.5% for the Fislis, Sevelen, Horn, Speyer 2.2 and Speyer 6S, respectively. The reported $K_{des\ FOC}$ ranged from 31.3 to 59.1. According to the results of desorption cycle, the adsorption of MS is potentially reversible.

I. MATERIALS AND METHODS

A. Materials

1	**Test Chemical**	5-Chloro-2-methylsulfonyl thiazole
	Description:	Brown crystals
	Lot/Batch:	231PAL052

	Purity:	98.7%
	CAS#:	
	Stability of Compound:	The test item was stable in the application solution during the treatment of the soil samples
2	**Soil:**	A summary of the physical and chemical properties of the soils is provided in **Table 1**.

Table 1: Soil Physiochemical Properties

Soil designation	soil type*	% sand	% silt	%clay	% OC	CEC (meq/ 100g)	pH
Fislis	silt loam	8.0	65.6	26.4	2.13	23	6.8
Sevelen	sandy loam	53.5	37.0	9.5	1.61	9	7.4
Horn	loam	38.7	36.2	25.1	2.36	22	7.2
Speyer 2.2	loamy sand	81.4	12.2	6.4	2.16	10	5.4
Speyer 6S	clay	21.9	36.0	42.1	1.75	22	7.2

* : USDA classification
% OC: percentage organic carbon
CEC :cationic exchange capacity

B. Study design

1. Experimental conditions

An adsorption/desorption kinetics experiment was performed to determine equilibrium time. A stock solution of 11.19 mg MS/L was prepared in acetonitrile and was diluted in 0.01M $CaCl_2$ solution to obtain a spike solution of 10.0 mg/L. The slurries (approximately 10 g soil and 18 mL 0.01 M $CaCl_2$ solution were equilibrated at 20± 2°C in the dark for three days prior to spiking. The adsorption stage of the kinetic experiment was initiated by adding a weighted volume of approximately 2 mL of spike solution to the pre-equilibrated soil slurries. A control without soil and a blank sample of each soil were also prepared. The samples were equilibrated on a roller mixer at 20± 2°C in the dark. The slurries were centrifuged at 3, 6, 24 and 48 hours. A 1.8 mL aliquot of the supernatant was sampled for analysis. After 48 hours of equilibration, the remaining supernatant of each test system was decanted and weighted. The pH of the supernatants was measured. The remaining soil of one vessel of Fislis, Sevelen and Horn test system was stored for analysis. The desorption stage of the kinetic experiment was initiated by adding equal weight of fresh 0.01 M $CaCl_2$ to decanted soil samples and equilibrated on a roller mixer. At the desorption sampling times (3, 6, and 23 hours), the slurries were centrifuged. A 1.8 mL aliquot of supernatant was sampled for analysis. After the final desorption sampling step, the remaining supernatant of the Fislis, Sevelen and Horn soils was decanted and weighted. Mass balances were determined for Fislis, Sevelen and Horn test system.

For the adsorption/desorption isotherm experiment, a stock solution of 24.77 mg MS in 10 mL

50/50 (v/v) acetonitrile/Milli-Q water was prepared (2477 mg/L). A series of spike solutions of 1, 5, 10 and 25 mg MS/L were prepared by dilution of this stock solution in 0.01M CaCl2 solution. Additionally, a spike solution of 10.17 mg MS in 100 mL 0.01M CaCl2 solution was prepared (102 mg/L). The slurries (approximately 10 g soil and 18 mL 0.01 M CaCl2 solution in polypropylene tubes) were equilibrated overnight on a roller mixer at 20 ± 2°C in the dark. After equilibration, the samples were spiked with 2 mL spike solution to obtain final MS concentrations in the test solutions of 0.1, 0.5, 1, 2.5 and 10 mg/L. Control samples without soil at each concentration level were included, as well as a blank sample for each soil. All experiments were performed at 20 ± 2°C in the dark. After 24 hours of contact time on a shaker, the soil slurries were removed from the shaker and centrifuged for 5 minutes at 540 g. Aliquots of 1.8 mL were taken and stored at ≤-15°C until analysis. The supernatants were decanted and weighed. The decanted supernatant was replaced by an approximately equal, known volume of fresh 0.01 M CaCl2 solution. The test system slurries were mixed well and placed back on a shaker at 20 ± 2°C. After a desorption period of 24 hours, the test system slurries were centrifuged for 5 minutes at 540 g. Aliquots of 1.8 mL were taken and stored at ≤-15°C until analysis. After decantation, the Fislis, Sevelen and Horn soils were also stored at ≤-15°C and were later extracted with 50/50 (v/v) acetonitrile/water (20 mL). The extracts were analyzed by LC/MS.

2. Description of analytical procedure

The test substance concentrations in the solutions were determined by means of an LC/MS validated method. The limit of quantification (LOQ) was assessed at 0.05 mg/l in 0.01M aqueous CaCl2.

II. RESULTS AND DISCUSSION

A. Mass Balance

The recovery for each sample was determined as the sum of the adsorption solutions and the soil extracts (non-extractables not included). The mass balances of the kinetic experiment were in the range of 77-86%. The mass balances of the isotherm experiment were in the range of 95-106%. The recovery of the control samples was in the range of 100-108%.

B. Findings

According to the results of the kinetic experiment, the adsorption equilibrium was reached after approximately 24 hours. The amount of MS adsorbed to soil was between 23% and 32%. No clear desorption equilibrium was reached. The pH of the supernatants ranged from 7.1 to 7.3 after adsorption and from 6.6 to 6.7 after desorption.

For the isotherm experiment, sorption parameters for both linear and Freudlich isotherms (Kd, Koc, KF, KFOC and 1/n) for the adsorption phase and desorption phase have been determined and reported in **Table 2**. The pH of the supernatants ranged from 6.9 to 7.5 after adsorption and from 6.8 to 7.3 after desorption.

Table 2: Adsorption Characteristics of MS on Soil

Parameters		**Soil** Fislis	Sevelen	Horn	Speyer 2.2	Speyer 6S	**Mean**
Texture		Silt loam	Sandy loam	Loam	Loamy sand	Clay	---
% Organic carbon		2.13	1.61	2.36	2.16	1.75	---
% Organic matter		3.67	2.78	4.07	3.72	3.002	---
pH ($CaCl_2$)		6.75	7.36	7.23	5.4	7.2	---
K_d	[mL/g]	0.306	0.282	0.649	0.568	0.884	**0.538**
K_{OC}	[mL/g]	14.3	17.5	27.5	26.3	50.5	**27.2**
K_F	[mL/g]	0.298	0.183	0.698	0.537	0.830	**0.509**
K_{FOC}	[mL/g]	14.0	11.4	29.6	24.9	47.4	**25.5**
1/n	-	0.881	0.899	0.914	1.05	0.986	**0.947**
r^2	-	0.9982	0.9987	0.9991	0.9997	1.000	**-**
$K_{des, F}$	[mL/g]	0.667	0.603	1.31	1.13	1.03	**0.95**
$K_{des, FOC}$	[mL/g]	31.3	37.4	55.4	52.2	59.1	**47.1**
1/n	-	1.69	1.34	1.05	1.03	1.12	**1.25**
r^2	-	0.998	0.994	0.974	0.999	0.998	**-**

III. CONCLUSIONS

MS is estimated to be very mobile in soil. The estimated mean $K_{ads\ FOC}$ and $K_{des\ FOC}$ were 25.5 and 47 mL/g, respectively.